Glyphosate Residues In Alberta's Atmospheric Deposition, Soils And Surface Waters

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Glyphosate Residues In Alberta's Atmospheric Deposition, Soils And Surface Waters

Prepared by:

Dave Humphries[1], Gary Byrtus[2], and Anne-Marie Anderson[2]

Prepared for:

Water Research Users Group
Alberta Environment

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[1] Trace Organics Laboratory, Alberta Research Council, Vegreville, Alberta
[2] Environmental Monitoring and Evaluation Branch, Alberta Environment, Edmonton, Alberta

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Any comments, questions, or suggestions regarding the content of this document may be directed to:

Environmental Monitoring and Evaluation Branch
Alberta Environment
10th Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Phone: (780) 427-6278
Fax: (780) 422-6712

Additional copies of this document may be obtained by contacting:

Information Centre
Alberta Environment
Main Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Phone: (780) 427-2700
Fax: (780) 422-4086
Email: env.infocent@gov.ab.ca

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EXECUTIVE SUMMARY

Glyphosate is a non-selective herbicide used for the control of annual and perennial grasses and broadleaf weeds. Registered for use in Canada in 1974, it is currently registered and used in over 125 countries. With annual sales in Alberta (1998) exceeding 2.6 million kg of active ingredient, it is by far the most commonly used pesticide in the province. Long considered by scientists and farmers around the world as an effective and environmentally friendly herbicide, recent studies have shown some persistence and mobility in the environment.

This study was designed to explore some of the pathways of glyphosate to surface waters such as atmospheric deposition, emissions during spraying, and persistence in soil; the study also included the monitoring of water from selected streams and wetlands.

The sampling year 2002 proved to be a difficult year to undertake a glyphosate residue study due to environmental factors. The severe drought conditions in east central Alberta hampered canola growth and subsequently greatly reduced the amount of glyphosate used in this growing and sampling season. Despite the drought and reduced usage, glyphosate was found in many environmental samples.

Atmospheric deposition was measured at three sites in east central Alberta. Rainfall and particulate matter were collected as total deposition at seven-day intervals throughout the growing season. The three precipitation sites had glyphosate detections throughout the sampling time period. Glyphosate deposition rates ranged from <0.001 to 1.51 $\mu g/m^2/day$.

Volatile and particulate emissions of glyphosate were measured before and after the spraying of a canola field with Roundup®. This study component was conducted in the Mannville area on a field with glyphosate tolerant canola. Pre-event air samples were taken two weeks prior to spraying. Post-event air sampling was conducted for 24-hour periods beginning at 1-hour post spray, 25-hour post spray and 49-hour post spray. Glyphosate was not detected in any of the air samples collected with polyurethane foam (PUF) samples but it was detected in some of the particulate samples. The detection of glyphosate in soil samples 10 months after spraying was indicative of some persistence.

Glyphosate was detected in most of the wetlands and streams sampled for this project. Concentrations were generally close to the detection limit (0.2 µg/L). Higher levels were recorded at some sites: Wetland #5 sample (1.066 µg/L), two Haynes Creek samples (1.105 and 0.425 µg/L) and a sample from the St. Mary's River Irrigation District (6.079 µg/L).

This study determined that glyphosate is transported in association with particulate matter (dust) and not as vapour. Detections in precipitation are more likely due to glyphosate associated with dust particles being washed down with rain than to glyphosate dissolved in rain.

A follow up study is recommended to document residue levels in a year where glyphosate use and moisture patterns are closer to normal for that part of the province. As well, the persistence of glyphosate in soils warrants further studies under different climatic conditions.

ACKNOWLEDGEMENTS

This project had complex technical and logistic demands that required teamwork from staff at the Alberta Research Council-Vegreville (ARC), Alberta Environment (AENV), and Alberta Agriculture Food and Rural Development (AAFRD). These three organizations were involved in the design of the study and in field-sampling aspects and contributed to the production of the technical report and interpretation of results.

This program was funded by the Water Research User Group (WRUG), Alberta Environment (AENV) and Alberta Agriculture, Food and Rural Development, and with 'in-kind work" provided by Alberta Research Council – Vegreville, AENV and AAFRD.

John Dach and Grant Prill (ARC) provided assistance in the design of the spray event study. Grant provided access to his land and crop and John installed the sampling equipment and collected the air samples. Grant also supplied the location for the Mannville precipitation site, and carried out the weekly collections.

Kristina Stefanizyn (ARC) maintained the Vegreville atmospheric deposition site, conducted the PUF spiking study, the field stability study, and the comparison of the suitability of glass/plastic sample bottles. She also performed all chemical analyses.

Mike Bilyk, and Mike Smilski (AENV) conducted the wetlands and stream sampling and the atmospheric deposition sampling at the Parlby site.

Jamie Wuite (AAFRD) arranged for partial financial support for this project and reviewed the report. Mike Sajjad (AAFRD) sampled wetlands and streams.

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1.0 BACKGROUND

Glyphosate is a broad spectrum, relatively non-selective herbicide that is applied as a post-emergent spray to target vegetation. Uptake is through the foliage, from where the herbicide is translocated through the plant. The major usages are as post-emergent or pre-harvest weed killer in herbicide tolerant crops, as a general-purpose weed killer used prior to seeding, and as an alternative to tillage for weed control in summer fallow.

With over 2.6 million kg of active ingredient (kg ai) sold annually, glyphosate is the most commonly used pesticide in Alberta (AENV 2001). Glyphosate is sold in Alberta as Roundup® (Monsanto) and Touchdown® (Zeneca), as well as several other products (AAFRD 2002).

Table 1 Province of Alberta glyphosate sales – 1998 (AENV 2001)

Usage	kg ai	Percentage
Agriculture	2,626,649	97.94%
Domestic	6,081	0.23%
Commercial/Industrial	48,976	1.83%
Forestry	41,431	1.50%

Glyphosate is very soluble in water, but because of its strong sorption to soils, its presence in surface waters was considered unlikely. Studies conducted elsewhere describe half-lives in water of a few days to two weeks as fairly conservative estimates (Giesy et al. 2000). The principal processes for loss in waters are adsorption to suspended particulate matter or sediments and microbiological degradation. Additional studies have shown glyphosate in soil to be reduced by 50% in 45-60 days with further reduction to 6-18% within in 365 days (Goldsborough, 1993).

In Alberta, several efforts have been made over the years to determine glyphosate in environmental samples and to improve analytical capabilities:

- In 1998 Alberta Environment sampled 11 streams throughout Alberta for residues of glyphosate and its degradation product, aminomethylphosphonic acid (AMPA). No detections were reported but the detection levels for that project were high (DL>5 µg/L and >10 µg/L) relative to environmental concentrations of routinely detected pesticides (G. Byrtus, unpublished data).
- In 1999, Alberta Agriculture detected glyphosate in runoff from a field that had been treated with Roundup® (J. Wuite, AAFRD, pers. comm.).
- In 1999 Alberta Research Council – Vegreville (ARC) developed and implemented a new analytical method (Appendix 1) for glyphosate and AMPA with detection levels of 0.2 µg/L and 1.0 µg/L, respectively. Agricultural stream samples analyzed as part of ARC method development had a high incidence of glyphosate detection.

- In 2000, a study on wetlands in the Aspen Parkland Region (Anderson et al. 2002) revealed frequent detections and relatively high levels of glyphosate in wetland water and precipitation, using the ARC technology.
- In another 2000 study, glyphosate was also detected in rain samples (G. Byrtus, unpublished data).

The scientific name for glyphosate is N- (phosphonomethyl)glycine and Chemical Abstract Number is 1071-83-6. Glyphosate structural information and characteristics, and AMPA structural information and characteristics are given in Appendix 1.

A third compound, glufosinate, was also analyzed in precipitation and surface water samples collected in this study. This compound was added to the study because it is structurally similar to glyphosate, used for the same general purpose (weed control in herbicide tolerant crops) and is analyzed in the same process stream as glyphosate and AMPA using the same sample and derivatization technique. Glufosinate is sold in Alberta as Liberty® and is used with Liberty-Link® canola, a glufosinate tolerant canola similar to Roundup® tolerant canola (AAFRD 2002). The volume of glufosinate sold in Alberta is quite low (64,000 kg ai) compared to glyphosate sales (Byrtus 2002). Structure and characteristics for glufosinate are also given in Appendix 1.

2.0 INTRODUCTION

Previous sampling programs (Reynolds 1989, Franz 1997, Byrtus, unpublished data, Anderson et al. 2002) identify glyphosate as a potentially widespread contaminant of surface waters.

The general objectives of this study were to build on previous monitoring programs to improve our understanding of glyphosate distribution in surface waters and to obtain further information on suspected pathways for glyphosate entry into surface waters. More specifically, this study provides information on:

- The presence of glyphosate, AMPA and glufosinate in atmospheric deposition from three locations in the Aspen Parkland of Alberta;
- The movement of glyphosate into the air during spraying of a Roundup-ready canola field;
- The persistence of glyphosate and AMPA in the soil from that field; and
- The occurrence of glyphosate, AMPA and glufosinate in a selection of wetlands and agricultural streams.

These study components are discussed in the body of this report and study sites are illustrated in Appendices 2, 3, 4, 5 and 6.

Two critical aspects of sample handling were investigated in parallel to field studies:

- The suitability of glass bottles for glyphosate sampling was investigated because there are instances where it is advantageous to collect single samples. Plastic bottles have been recommended for routine sampling of glyphosate, whereas glass bottles are prescribed for all other pesticides routinely monitored in Alberta.
- The degradation of glyphosate, AMPA and glufosinate in sample bottles exposed to field conditions was documented. This information will help optimize the collection of atmospheric deposition samples which are generally retrieved every 7 or 14 days.

These study components are discussed in Appendices 7 and 8.

In addition to routine laboratory and field quality assurance and quality control measures, QA/QC samples comprising blanks, duplicates and spikes were an integral part of the sampling program and results are presented in Appendix 9.

3.0 ATMOSPHERIC DEPOSITION

3.1 Objective

The objective of this study component was to measure concentrations and loadings of glyphosate and AMPA in atmospheric deposition (wet + dry) collected at three locations in the Aspen Parkland over the growing season.

3.2 Methods

3.2.1 Site Location and Description

Three sites were selected in the Aspen Parkland Region for this study: Mannville, Vegreville, and Parlby (Figure 1).

- The Vegreville site is located in the County of Minburn (SW 23-52-15-W4; Latitude and Longitude Coordinates: N53° 30' 18.9" and W112° 05' 33.2", respectively). It is located on the Alberta Research Council (ARC) property, which is situated on the west side of the Town of Vegreville. West of the sampling site are ARC field plots which are used for agricultural studies. East of the site is a hay field which extends for 1.5 km before the start of the urban area. South of the site are the building facilities of ARC followed by a large slough area. One km north of the site is Highway 16A, and cattle penning facilities are situated between the highway and the site. Farming in the Vegreville area is typified by mixed farming practices. No fields in close proximity (minimum 0.5 km radius) to this site were treated with glyphosate for either pre-seeding weed control, post-emergent or pre-harvest weed control.

- The Mannville site is located in the County of Minburn (SW 24-50-8-4, Latitude and Longitude Coordinates: N53° 24' 24.1" and W111° 06' 54.7", respectively) on a farm 8 km west of Mannville and 14 km east of the Town of Vermilion. It is near the north side of the quarter section about 0.3 km from the western boundary. The site is quite elevated compared to the surrounding area with a line of sight of about 16 km to the north and west, and 3 –16 km to the north and east. The highest spot in the area is a ridge or hill running east and west about 100 metres to the south. The sample collection spot is on the west side of a 2 ha yard site and is on the edge of cropland. It is completely open to the west and north where prevailing winds originate, and is not adversely affected by natural trees or shelterbelts on this side. Shelterbelts to the northeast would affect the movement of air-borne particles. Farming practices in the surrounding area are now predominately zero till, continuous cropping operations. Herbicide usage has increased substantially to allow these practices to be followed. Glyphosate usage in particular has increased due to pre-seeding, post-emergent and pre-harvest weed control.

  Recent glyphosate applications in the vicinity of this site include pre-seeding weed control in spring 2001 on the quarter sections immediately to the north and west and annual pre-seed and pre-harvest weed control on the next section to the west.

Figure 1 Map showing location of sampling sites

- The Parlby site is located in the County of Lacombe (NE 33-40-22 W4, Latitude and Longitude Coordinates: N52° 29' 38" and W113° 06' 28", respectively), approximately 2 km north of the Village of Mirror. It is situated adjacent to Parlby Creek near a Water Survey of Canada (WSC) flow gauge and Alberta Environment weather station. The quarter section where the precipitation collector is located is in pastureland and bush, and so are the surrounding quarter sections. The closest cultivated land is ½ km to the east. Nearby glyphosate applications are not documented.

3.2.2 Atmospheric Deposition Sample Collection and Processing

Atmospheric deposition of glyphosate was collected with bulk precipitation collectors designed after a prototype developed by Agriculture and Agri-Food Canada, Lethbridge (Hill et al. 2001). The sample collector is a 26 cm diameter plastic funnel draining into a 4 L plastic bottle wrapped in aluminum foil. Collectors were placed at ground level, secured with wooden stakes and elastic cords (see Appendix 3 for picture). The total area sampled represented 0.0531 m^2.

Samples were collected every seven days with the occasional fourteen-day period during dry spells.

At the end of the sampling period each funnel was rinsed with 125 mL of soil extraction solution (0.25M NH_4OH / 0.10M KH_2PO_4). This solution helps rinse any particulate matter (dust fall) left on the funnel surface and ensures the extraction of the compounds of interest from the particulate matter in the samples (similar to analyzing soil samples). Sample volume was measured and corrected for the addition of rinse solution. These samples were then analyzed following methods described for water (Appendix 1).

Atmospheric deposition of glyphosate is reported as concentration (µg/L) and as loading (µg/m^2/day).

3.3 Results and Discussion

AMPA and glufosinate were not detected in any of the atmospheric deposition samples collected at the three sites. The absence of detection of AMPA could be due to the rapid degradation of this compound (Appendix 7) and to its higher detection limits (1 µg/L) than glyphosate. Similarly, the higher detection limit for glufosinate (2 µg/L) and its low relative usage may also account for its lack of detections.

In contrast to AMPA and glufosinate, glyphosate was detected at the three sites; results of glyphosate measurements are shown in Table 2 and Figure 2. Although the method detection limit for glyphosate is 0.2 µg/L, it is possible to measure much lower concentrations of glyphosate when matrix interference is not an issue; hence several reported concentrations for glyphosate are well below 0.2 µg/L (e.g., Tables 2 and 3).

At the Vegreville site, eight out of the eleven samples had measurable glyphosate concentrations, and this site had the most consistent pattern of glyphosate detections over the sampling period.

Glyphosate concentrations and loadings appear to be negatively related to precipitation in that greater amounts of precipitation generally meant lower glyphosate concentrations and deposition rates (Figure 2). Several high precipitation events (11.4 mm, 21.7 mm, and 4.5 mm) had glyphosate concentrations below the detection limit. The highest deposition rate (1.26 µg/m^2/day) was associated with significant precipitation, but occurred immediately following 14 days of very dry weather (only 0.5 mm in 2 weeks). The dry weather may have resulted in more dust in the atmosphere.

Glyphosate was detected in four of the eight samples taken from the Mannville site. With the exception of the final sampling event of late July – early August, glyphosate loading increased with precipitation. This is in contrast with the observations for the Vegreville site and suggests that the relationship between precipitation and glyphosate loading is not a simple one. Assuming that glyphosate in the air is associated with dust, the amount of dust in the air would determine the atmospheric loading rather than the amount of precipitation received and concentrations would be expected to be relatively independent of the rainfall amount. For the final sampling

Table 2 Glyphosate concentration and loading in atmospheric deposition

Sampling Period			Glyphosate		Precipitation	
Start Date	End Date	# Days	Loading µg/m^2/day	Concentration µg/L	in L	in mm
Vegreville Station						
15-May	22-May	7	0.186	0.42	0.165	3
22-May	29-May	7	0.242	1.8	0.050	0.9
29-May	5-Jun	7	0.188	2.8	0.025	0.5
5-Jun	12-Jun	7	0.377	5.6	0.025	0.5
12-Jun	19-Jun	7	0.807	0.8	0.375	0.68
19-Jun	26-Jun	7	0.402	0.65	0.230	4.2
26-Jun	3-Jul	7	<0.034	<0.02	0.630	11.4
3-Jul	17-Jul	14	0.108	3.2	0.025	0.5
17-Jul	24-Jul	7	1.260	1.09	0.430	7.8
24-Jul	31-Jul	7	<0.034	<0.05	0.250	4.5
31-Jul	7-Aug	7	<0.032	<0.01	1.200	21.7
Mannville Station						
15-May	22-May	7	0.080	0.2	0.025	0.5
22-May	29-May	7	<0.027	<0.67	0.015	0.3
29-May	5-Jun	7	0.430	1.6	0.100	1.8
5-Jun	12-Jun	7	<0.001	<0.01	0.000	0
12-Jun	19-Jun	7	0.540	0.98	0.205	3.7
19-Jun	3-Jul	14	<0.013	<0.10	0.100	1.8
3-Jul	23-Jul	12	0.449	0.26	1.100	19.9
23-Jul	7-Aug	15	<0.012	<0.006	1.580	28.6
Parlby Station						
15-May	22-May	7	0.297	0.26	0.425	7.7
22-May	29-May	7	<0.027	<0.33	0.030	0.5
29-May	5-Jun	7	0.565	0.84	0.250	4.5
5-Jun	12-Jun	7	<0.027	<0.40	0.025	0.5
12-Jun	19-Jun	7	<0.025	<0.03	0.315	5.7
19-Jun	26-Jun	7	<0.026	<0.28	0.035	0.6
26-Jun	3-Jul	7	1.510	1.18	0.475	8.6
3-Jul	17-Jul	14	0.174	0.74	0.175	3.2
17-Jul	31-Jul	14	<0.013	<0.005	1.990	36.1

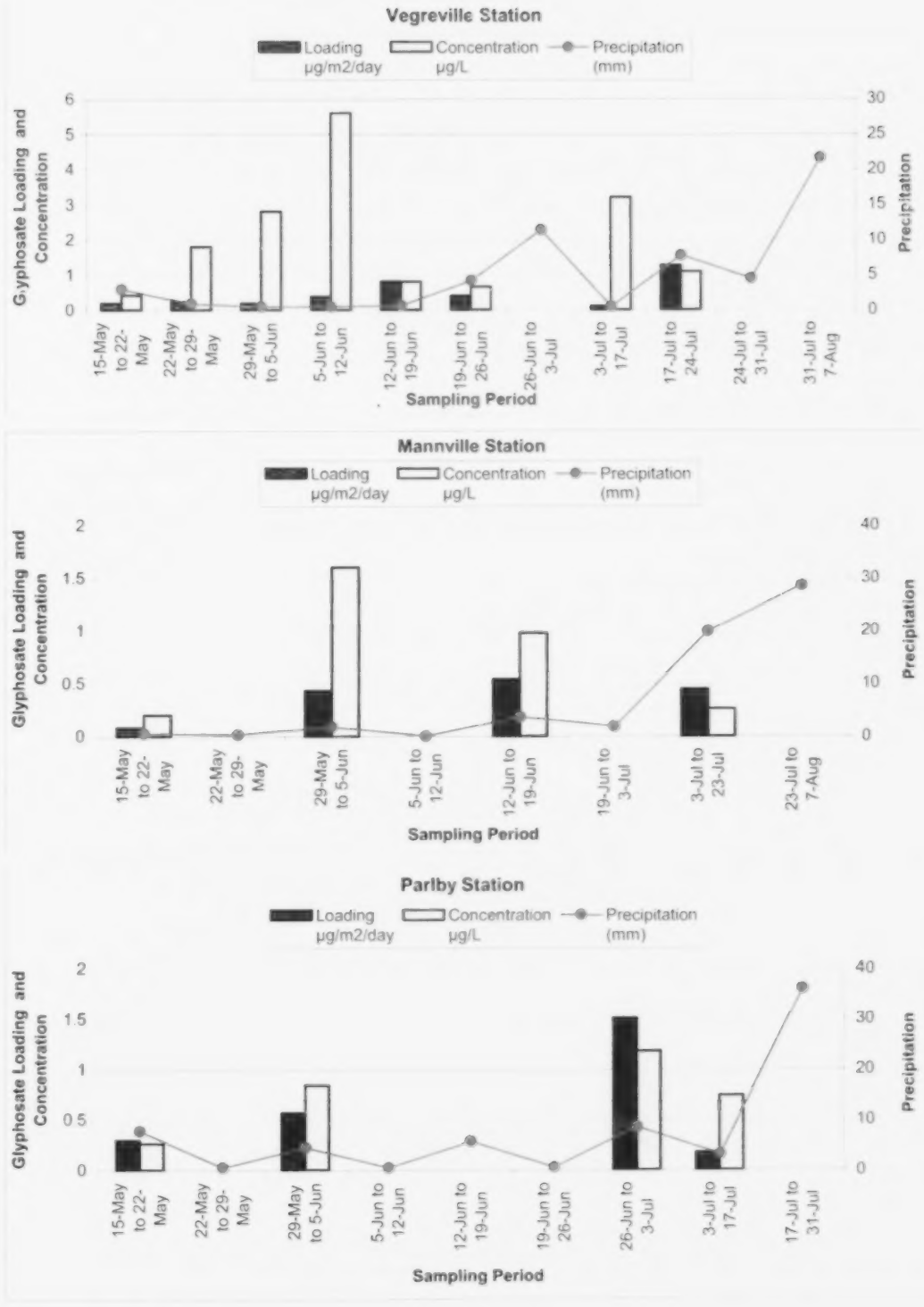

Figure 2 Glyphosate in atmospheric deposition

(July 23 – August 7) glyphosate concentration was less than the method detection limit, possibly because spraying for this area was completed, or because precipitation during the previous sampling events reduced the amount of dust in the air.

The Parlby site showed little in the way of trends. Sometimes higher precipitation amounts resulted in higher glyphosate loading, similar to the Mannville site. At other times, greater amounts of precipitation resulted in lower glyphosate loadings, similar to the Vegreville site. For the final sampling (July 17 to July 31) the glyphosate concentration was less than the method detection limit. The reasons for this situation may be similar to those cited for the Mannville site.

Despite the greatly reduced usage of glyphosate compared to normal application years, glyphosate was still detected on a regular basis at all three sampling locations. The Vegreville site had the highest incidence of detections with only 3 of 11 sampling dates having concentrations below the detection limit. The highest daily load (1.51 $\mu g/m^2$/day for the period 26 June to 3 July) was calculated for the Parlby site.

In 2002, glyphosate was detected during the first sampling event (May 15 to May 22) at all three sampling sites. Further studies should start the sampling season earlier; perhaps before the snow cover disappears. Soil analyses from the field that was sprayed with glyphosate (Section 4.3.2) indicate that glyphosate can persist in soil over winter. In addition to possible losses of glyphosate with surface runoff during spring melt, this soil-bound glyphosate could become a source of airborne glyphosate in early spring before spraying begins.

Results of glyphosate analysis reported in Anderson et al. (2002) in precipitation at Vegreville during 2000 are given in Table 3. The glyphosate loading is similar to that reported in this study. Concentrations of glyphosate in 2000 were much lower than in 2002, this may be related to the relatively higher amount of precipitation received in 2000.

Glyphosate was detected in atmospheric deposition in July at the three sites sampled in 2002, but not in 2000. This may be due to the drier conditions in 2002, resulting in more dust in the atmosphere.

Table 3 Glyphosate 2000 atmospheric deposition results - Vegreville site (Anderson et al. 2002)

Start Date	End Date	# Days	Glyphosate		Precipitation mm
			Loading $\mu g/m^2$/day	Concentration µg/L	
30-May	9-Jun	10	0.249	0.07	36.2
9-Jun	12-Jun	3	0.310	0.06	16.0
12-Jun	19-Jun	7	0.227	0.20	7.8
19-Jun	4-Jul	15	0.078	0.22	5.4
4-Jul	7-Jul	3	nd	nd	14.8
7-Jul	11-Jul	4	nd	nd	21.6
11-Jul	18-Jul	7	nd	nd	15.0

4.0 SPRAY EVENT STUDY

4.1 Objectives

The objective of this study component was to measure glyphosate in air (vapour and particulate samples) and soil samples following the application of Roundup® to a canola field. AMPA was analyzed in soil samples only.

4.2 Methods

4.2.1 Study Design

A glyphosate-tolerant canola field (Appendix 4) was scheduled to be sprayed with Roundup® twice in the 2002 growing season at recommended application rates. The first spraying was scheduled approximately 2 weeks after seeding and the second spraying 3 to 4 weeks after the first spraying (dependant upon conditions and weed growth). Application rates for both spraying events were 0.5 L/acre (440 g active/ha). Air samples (both vapour and particulate), soil samples and runoff samples were to be collected to obtain data on glyphosate and AMPA losses following spraying.

The lack of moisture in the area delayed the initial spraying and the continued drought eliminated the need for a second spraying. No field runoff occurred in 2002 or 2003.

4.2.2 Air Sampling

Volatile glyphosate was collected on a polyurethane foam plug (PUF) and particulate glyphosate on a filter paper using two types of air sampling devices (Appendix 5).

1. VAPS (Versatile Air Pollutant Sampler)

    - The VAPS is an assembly of components that allows the simultaneous measurement of a variety of air quality parametres
    - Air passes through a 10-µm inlet to remove and discard particles larger than 10 µm while quantitatively transmitting particles less than 10 µm to the virtual impactor.
    - Larger particles entering the virtual impactor of the VAPS flow downward at a rate of 2 litres per minute and collect on a Zefluor filter (47 mm with a 2 µm porosity). Smaller particles follow the two airstreams that flow at a rate of 15 litres per minute and collect on Zefluor filters (47 mm diameter) with a 2 µm porosity).
    - The filtered air passes through a polyurethane foam (PUF) trap (100 mm x 25 mm), which collects the vapour form of glyphosate.
    - The VAPS sampler allows for separation of particles into three size classes: >10 µm, 10-2 µm, and <2 µm.

2. Model GPS1 PUF Sampler Particulate and Vapour Collection System

- The Model GPS1 is a high volume air sampling system designed to collect suspended, airborne particulates and trap airborne pesticide vapours at flow rates up to 280 litres per minute.
- Air passes through an upper chamber that supports the airborne particulate filter media (100 mm with a 3 μm porosity) in a circular filter holder.
- The filtered air passes through the lower chamber, which encapsulates a glass cartridge containing the polyurethane foam (75 mm x 63.5 mm).
- The GPS1 sampler collects all particles without any size separation.

The GPS1 and VAPS samplers were set up within 2 metres of each other on a grassy outcrop in the sprayed field (see pictures Appendix 4).

Initial (background) soil and air sampling was scheduled one to two weeks prior to the spray event. An exact pre-spray sample time could not be set because the actual spraying was dependant upon weather conditions (wind, rain), growth of crop (canola) and weed growth. The actual pre-event collection occurred on June 7, 2002, two weeks before the spraying that occurred on June 21, 2002 and was carried out over 24 consecutive hours.

Post-event sampling was carried out in three consecutive 24-hour periods, starting 1, 25, and 49 hours after completion of spraying.

4.2.3 Soil Sample Collection and Analysis

Field soil samples were collected and analyzed two weeks before spraying, 1 week, 4 months, 10 and 17 months after spraying. Samples were collected by taking surface soil (0-5 cm) at points along a transect to the east and another transect to the north of the air sampling equipment (see Appendix 4 for sampling diagram). The individual soil samples were combined and then sub-sampled for analysis (i.e., one sample per sample date).

Soil analysis was performed as per ARC Glyphosate in Soil Method (see Appendix 1).

4.3 Results and Discussion

4.3.1 Air Samples

During the entire sampling period winds were calm, daytime temperature ranged in the low to high 20°C, and conditions were dry.

Very little glyphosate was detected in air samples (Table 4). Only the three post-spray GPS filter samples yielded detections. No glyphosate was detected in any of the PUF samples (VAPS or GPS1). The volume of air sampled with the VAPS sampler was too small and in future, a longer

Table 4 Spray event results

Spray Event Sampling Summary							
Spray Event: 7-Jun-02							
Sampler	**Sample Type**	**Airflow** m^3	**Particulate** mg/filter	**Particulate/Airflow** mg/m^3	**Glyphosate** ng total	**Glyphosate** ng/m^3	**Glyphosate** ng/mg particulate
GPS	PUF	265.4			nd	-	-
	Filter		100	0.377	nd	-	-
VAPS	PUF-fine	20.8			nd	-	-
	Filter-fine-1		0.111	0.005	nd	-	-
	Filter-fine-2		0.083	0.004	nd	-	-
	PUF-coarse	3.1			nd	-	-
	Filter-coarse		0.499	0.161	nd	-	-
Temperature 6.0 – 20.0°C							
Spray Event: 21-Jun-02							
1-25 Hours After Spray Event							
GPS	PUF	229.7			nd	-	-
	Filter		151	0.657	185.0	0.81	1.23
VAPS	PUF-fine	21.2			nd	-	-
	Filter-fine-1		0.310	0.014	nd	-	-
	Filter-fine-2		0.361	0.017	nd	-	-
	PUF-coarse	3.2			nd	-	-
	Filter-coarse		0.723	0.226	nd	-	-
Temperature 8 – 25.0°C							
25-49 Hours After Spray Event							
GPS	PUF	242.8			nd	-	-
	Filter		101.0	0.416	216.0	0.89	2.14
VAPS	PUF-fine	20.7			nd	-	-
	Filter-fine-1		0.207	0.010	nd	-	-
	Filter-fine-2		0.231	0.011	nd	-	-
	PUF-coarse	3.2			nd	-	-
	Filter-coarse		0.537	0.168	nd	-	-
Temperature 12 – 27.0°C							
49-72 Hours After Spray Event							
GPS	PUF	238.1			nd	-	-
	Filter		99	0.416	176.2	0.74	1.78
VAPS	PUF-fine	21			nd	-	-
	Filter-fine-1		0.157		nd	-	-
	Filter-fine-2		0.153		nd	-	-
	PUF-coarse	3.2			nd	-	-
	Filter-coarse		0.599		nd	-	-
Temperature 15 – 28.0°C							

sampling period must be used if particle size distribution of glyphosate-bound materials is required. None of the VAPS filter samples had any glyphosate detections. The GPS1 collects all the dust without separating into particle sizes. The VAPS collects the particle sizes into <2 µm and 2 – 10 µm ranges, but discards any particles greater than 10 µm.

Detailed studies on atmospheric transport of glyphosate could benefit from glyphosate data for distinct particle size fractions that can be collected with the VAPS sampler, but for routine monitoring of glyphosate in air, the GPS1 sampler is preferable because it samples a larger volume.

The absence of glyphosate in the PUFs indicates that glyphosate is not released as the vapour form into the atmosphere but rather is carried by particulate matter.

4.3.2 Soil Sampling

Neither glyphosate nor AMPA were detected in the pre-event sample. Glyphosate was detected immediately (1 week) after spraying and was again detected four months (120 days) after spraying (Table 5). Because glyphosate was detected in the fall 2002 sample, additional soil samples were collected in April and October 2003, 280 and 510 days after spraying, respectively. Glyphosate was detected in April 2003, but not in October 2003.

In agricultural soils, half-lifes (DT_{50}) of glyphosate range from 1.7 to 197.3 days, but are typically less than 60 days depending upon edaphic and climatic conditions (Giesey et al. 2000). In this study, half the glyphosate remained after 120 days, but after 280 days the concentrations had not decreased any further. The first 120 days coincided with severe drought conditions and very low soil moisture levels. Much of the time elapsed between 120 and 280 days occurred during the winter, which in Alberta is typically associated with sub-zero temperatures. Drought and cold could have inhibited microbial degradation, which is the main cause of glyphosate breakdown (Giesey et al. 2000). The last samples taken in fall 2003, 510 days after spraying and following a comparatively moister growing season than in 2002, had no detectable trace of glyphosate.

These results indicate that glyphosate can persist relatively long in Alberta soils, possibly because of climatic conditions that inhibit microbial degradation. Further work is warranted to document breakdown rates of glyphosate for different soils typical of Alberta and under a variety of climatic conditions, including wet and warm periods.

Table 5 Spray event soil sample

Date	Type	Glyphosate	AMPA
		µg/g	µg/g
8-Jun-02	pre-event	<0.03	<0.15
27-Jun-02	post-event - spring 2002	1.67	<0.15
2-Nov-02	post-event - winter 2002	0.75	<0.15
12-Apr-03	post-event - spring, 2003	0.73	0.40
21-Oct-03	post-event - fall 2003	<0.03	<0.15

5.0 SURFACE WATERS

5.1 Objectives

The objective of this study component was to broaden the data base for glyphosate in Alberta surface waters by sampling some wetlands which had been sampled in 2000 and by initiating the sampling of agricultural streams, including some irrigation return flows.

5.2 Methods

5.2.1 Sampling Methods

Three wetlands (i.e., #5, 6, and 51 as referred to in Anderson et al. 2002) and 10 agricultural streams from the Alberta Environmentally Sustainable Agriculture (AESA) program were part of the sampling program (Figure 1). Battersea Drain, Drain S6, SMRID canal and New West Coulee receive return flows from irrigated land; the six remaining streams drain areas of dry-land farming.

Water samples from wetlands were collected on a weekly basis to correspond with the sampling schedule for atmospheric deposition; stream samples were collected on a flow-weighted basis in an attempt to capture effects of runoff. Stream samples are depth integrated grab samples, whereas wetland samples are composites of surface grab samples taken from several locations across the wetland.

Water samples were collected in 40 mL polyethylene bottles and were stored at 4°C until analyzed.

5.2.2 Laboratory Analyses

Samples were shaken to suspend particulate matter, concentrated 10 times under nitrogen and analyzed as per the method described in Appendix 1. Glyphosate, AMPA and glufosinate were analyzed in all surface water samples.

5.3 Results

AMPA and glufosinate (detection levels 1.0 µg/L) were not detected in any of the surface water samples. Glyphosate detections are summarized and presented in Table 6.

The pictures in Appendix 6 show the dramatic reduction in wetland size due to the drought conditions in east-central Alberta in 2002. Wetland #10 completely dried up by mid-June and no samples were collected from this site after June 12, 2002.

Glyphosate was detected at most sites (8 of 13), but only in 16 of the 74 samples collected (i.e., detection frequency of 22%). Most of the detections were in early spring (April), but glyphosate

Table 6 Glyphosate results for wetlands and streams

Location	Station Code	Sample Date	Glyphosate (µg/L)
Wetland #5 (near Mannville)	AB05EE1080	16-May-02	<0.2
		22-May-02	<0.2
		29-May-02	<0.2
		6-Jun-02	<0.2
		12-Jun-02	<0.2
		24-Jun-02	<0.2
		12-Jul-02	1.066
Wetland #10 (near Vegreville)	AB05EE0005	16-May-02	<0.2
		22-May-02	<0.2
		29-May-02	<0.2
		6-Jun-02	<0.2
		12-Jun-02	<0.2
Wetland #51 (near Stettler)	AB05CD0005	15-May-02	<0.2
		22-May-02	0.061
		29-May-02	0.254
		6-Jun-02	0.075
		12-Jun-02	<0.2
		19-Jun-02	<0.2
		3-Jul-02	0.286
Haynes Creek (near Clive)	AB05CD0520	15-Apr-02	1.105
		22-Apr-02	0.425
		30-Apr-02	<0.2
		15-May-02	<0.2
Threehills Creek	AB05CE0730	17-Apr-02	<0.2
		22-Apr-02	<0.2
		30-Apr-02	<0.2
		15-May-02	<0.2
Buffalo Creek At Hwy 41	AB05FE0060	22-Apr-02	<0.2
		30-Apr-02	<0.2
		08-May-02	<0.2
		21-May-02	<0.2
		07-Jun-02	<0.2
		17-Jun-02	<0.2
		19-Jun-02	<0.2
Renwick Creek near Three Hills	AB05CE0720	17-Apr-02	0.309
		22-Apr-02	<0.2
		30-Apr-02	<0.2
		15-May-02	<0.2
Battersea Drain (Picture Butte)	AB05AG0030	10-Apr-02	0.395
		25-Jun-02	0.236
		24-Jul-02	0.164
		27-Aug-02	<0.2
		24-Sep-02	<0.2
		07-Oct-02	<0.2
Drain 6 near Bow Island	AB05AJ0410	15-Apr-02	<0.2
		08-May-02	<0.2
		25-Jun-02	<0.2
		24-Jul-02	<0.2
		27-Aug-02	<0.2

Location	Station Code	Sample Date	Glyphosate (µg/L)
		24-Sep-02	<0.2
		07-Oct-02	<0.2
St. Mary's River Irrigation District (near Bow Island)	AB05AJ0420	25-Jun-02	6.079
		24-Jul-02	0.165
		27-Aug-02	<0.2
		24-Sep-02	<0.2
		07-Oct-02	<0.2
New West Coulee	AB05BN0790	10-Apr-02	0.219
		25-Jun-02	<0.2
		24-Jul-02	0.133
		27-Aug-02	<0.2
		24-Sep-02	<0.2
		07-Oct-02	<0.2
Ray Creek near Innisfail	AB05CE0710	17-Apr-02	<0.2
		22-Apr-02	<0.2
		30-Apr-02	<0.2
		15-May-02	<0.2
Rose Creek near Alderflats	AB05DE0010	16-Apr-02	0.196
		22-Apr-02	<0.2
		01-May-02	<0.2
		13-May-02	<0.2
		27-May-02	<0.2
		20-Jun-02	<0.2
		07-Aug-02	<0.2
		04-Sep-02	<0.2

was detected in several July samples. Detections in April most probably relate to the previous year of application. The levels detected were all low (being around the 0.2 µg/L detection level) with the exception of Wetland #5 sample July 12 (1.066 µg/L) and the two Haynes Creek samples collected on April 15 and April 22 (1.105 µg/L and 0.425 µg/L). The highest concentration, 6.079 µg/L, was measured in a June sample from the St. Mary Irrigation district.

Glyphosate has been reported in a number of surface water studies. Edwards et al. (1980) studied glyphosate residue movement in surface runoff from a small agricultural field in Ohio. Residues were detected in surface waters up to 2 months following application. More recent sampling programs confirm that glyphosate is a fairly common contaminant of surface waters. Studies conducted by the U.S. Geological Survey (Scribner et al. 2003) in 51 streams in 9 Midwestern States report a glyphosate detection frequency of 36% and maximum concentrations of 8.7 µg/L. Interestingly, AMPA was detected in 69% of the samples and a maximum concentration of 3.6 µg /L was recorded. In Quebec, glyphosate was detected in 38% of the samples taken from the Chibouet River in 2001 (Giroux 2002); concentrations were all low (maximum recorded : 0.2 µg /L). Compared to our findings, detection frequency is higher in the USGS and the Quebec study, but this is at least in part due to their lower detection limits. In both studies detection limit for glyphosate was 0.1 µg /L (compared to 0.2 µg /L in our study) and the USGS detection limit for AMPA was also 0.1 µg /L (compared to 1.0 µg /L in our study). The high detection limit for AMPA that is used in this study is the most likely reason why this degradation product was not detected in surface waters.

CCME (1999) has set glyphosate guidelines for the protection of aquatic life (65 µg/L), for treated drinking water (280 µg /L) and for livestock watering (280 µg /L). All concentrations reported in surface waters were well below these guidelines. This suggests that, despite the fact that glyphosate appears to occur commonly in surface waters, ambient concentrations of glyphosate, considered on their own, do not represent a threat to aquatic life or drinking water quality. However, it is relevant to refer to the QA/QC results presented in Appendix 9. These data indicate that glyphosate concentrations reported for surface waters are conservative, and ambient concentrations may be underestimated, particularly in waters rich in organic matter.

6.0 SUMMARY AND CONSIDERATIONS FOR FUTURE WORK

The year 2002 proved to be a poor year to conduct a glyphosate study due to the extensive drought that took place throughout Central Alberta. The use of glyphosate dropped dramatically because many farmers plowed under their crops instead of spraying to eliminate weeds. Similarly, in fall, farmers did not use glyphosate for pre-harvest weed control because weed growth was very limited or their crops were too poor to warrant chemical expenses.

Nevertheless, glyphosate was detected in many precipitation and surface water samples, confirming the common occurrence of the herbicide in these media. The study of air borne glyphosate during the spraying of a canola field showed that in the air glyphosate is associated with particles rather than vapour. Glyphosate applied in 2002 persisted until the following year of application in the soil of the treated field.

This study identified several areas that may warrant consideration in further work on glyphosate, AMPA and glufosinate.

- 2002 was a year of extreme drought in the study area and the importance of runoff from treated fields as a pathway for surface water contamination could not be assessed. Such study should be attempted in a year with higher soil moisture and precipitation. The persistence of glyphosate in freshwater sediments is also worthy of further investigation.

- Glyphosate detected in precipitation is probably associated with particulate matter. This could be verified by filtering samples and analyzing the filtrate and filter residue separately. In surface waters, the form in which glyphosate occurs could be confirmed in a similar manner.

- Lower method detection limits are needed in future monitoring of AMPA in atmospheric deposition and surface waters.

- Future precipitation studies that require the analysis of glyphosate and other pesticides could rely on glass containers, but the suitability of glass sample bottles for AMPA and glufosinate still needs to be determined.

- Future studies on atmospheric deposition on glyphosate and glufosinate need to involve collection intervals no longer than 14 days and preferably less; sampling of AMPA will need to be considerably more frequent considering the apparent rapid degradation of this breakdown product (Appendix 7).

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Appendix 1 Analytical Procedure

1.1 Analytical Method Summary

Glyphosate, AMPA, and glufosinate are derivatized directly from the aqueous medium using a 2:1 mixture of trifluoroacetic anhydride and heptafluorobutanol. The amine functional groups are derivatized with trifluoroacetic anhydride to form the corresponding trifluoroacetyl derivatives. The carboxyl and phosphonic acid functional groups are derivatized with heptafluorobutanol to form the corresponding heptafluorobutyl esters.

Soil samples are extracted with an ammonium hydroxide/phosphate buffer solution. The extract is cleaned up with activated carbon and derivatized as per the water sample method.

Identification and quantification is done by gas chromatography / mass spectrometry / Iontrap.

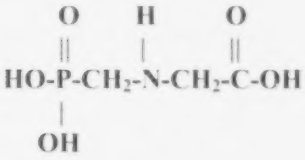
Detection limits for this analytical procedure are 0.2, 1.0 and 1.0 µg/L for glyphosate, AMPA, and glufosinate, respectively. Reliable measurements can sometimes be made in very clean matrices.

For full method details contact:

Analytical Chemistry
Trace Organic Laboratory
Alberta Research Council
P.O. Bag 4000
Vegreville, Alberta
T9C 1T4

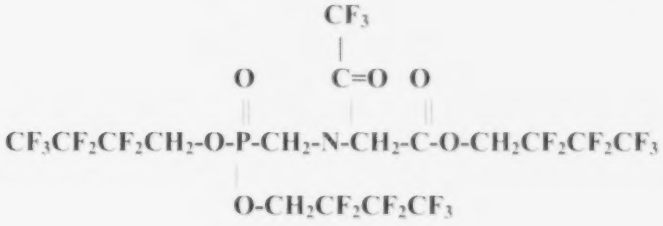
1.2 Structure and Characteristics of Glyphosate (British Crop Protection Council 1997)

GLYPHOSATE
MW 169



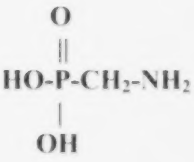
Chemical Abstracts Name: N-(phosphonomethyl)glycine
Solubility in water: 11.6g/L @ 25C

GLYPHOSATE DERIVATIVE
MW 811



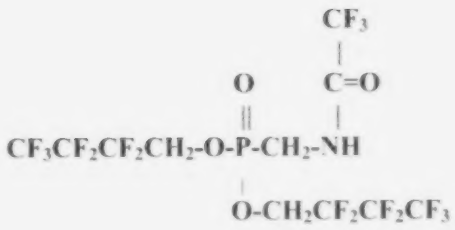
1.3 Structure and Characteristics of AMPA

AMPA
MW 111



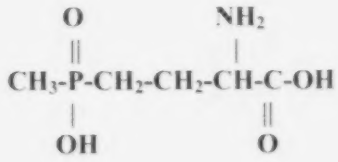
Chemical Abstracts Name: (aminomethyl)phosphonic acid

AMPA Derivative
MW 571



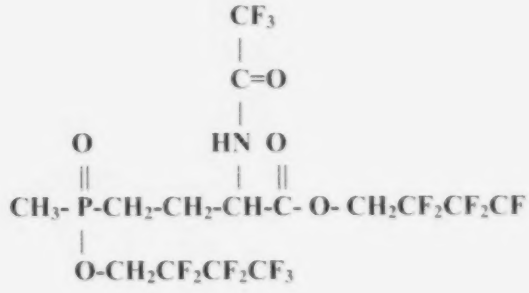
1.4 Structure and Characteristics of Glufosinate (British Crop Protection Council 1997)

GLUFOSINATE
MW 181



Chemical Abstracts Name: 2-amino-4-(hydroxymethylphosphinyl)butanoic acid

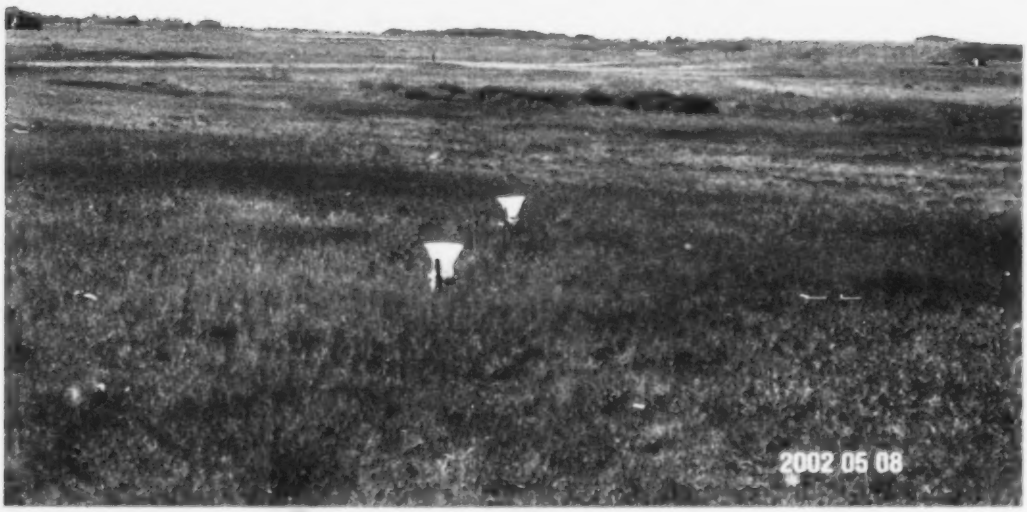
GLUFOSINATE Derivative
MW 641



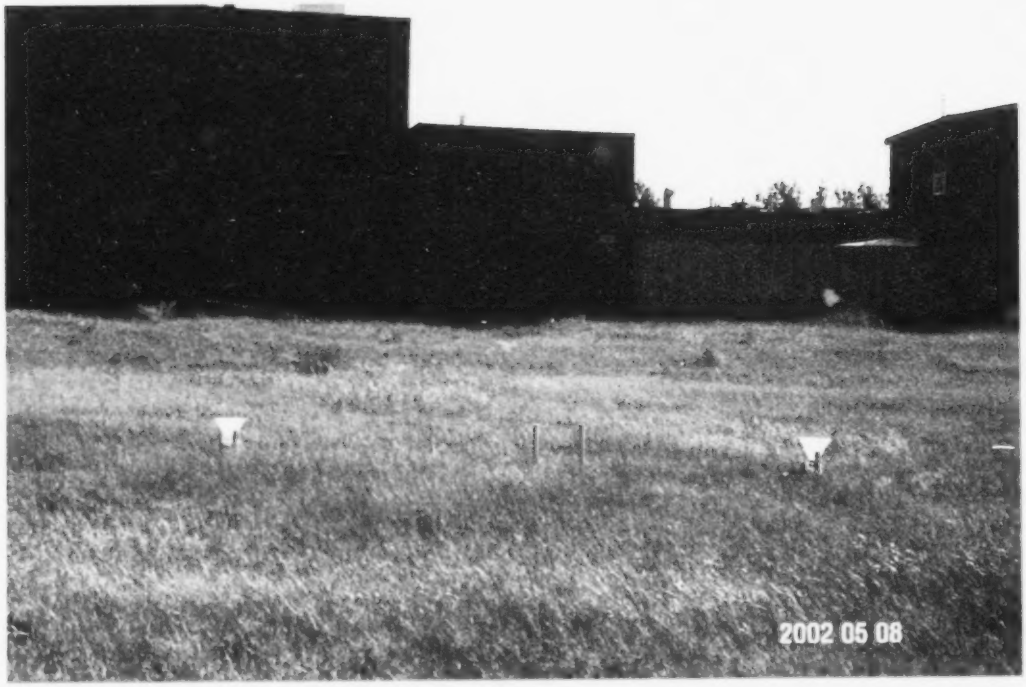
Appendix 2 Vegreville Atmospheric Deposition Site

Vegreville site: facing north

Vegreville site: facing west



Vegreville site: facing south

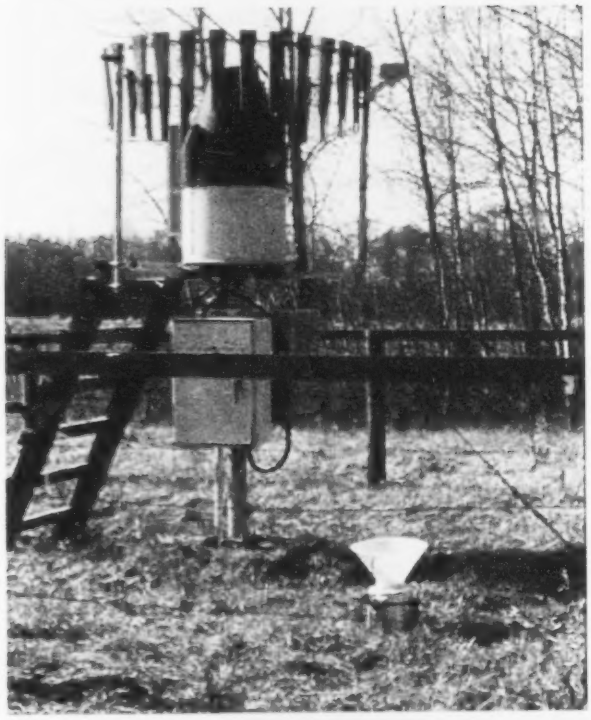


Vegreville site: facing east

Atmospheric Deposition sampling apparatus

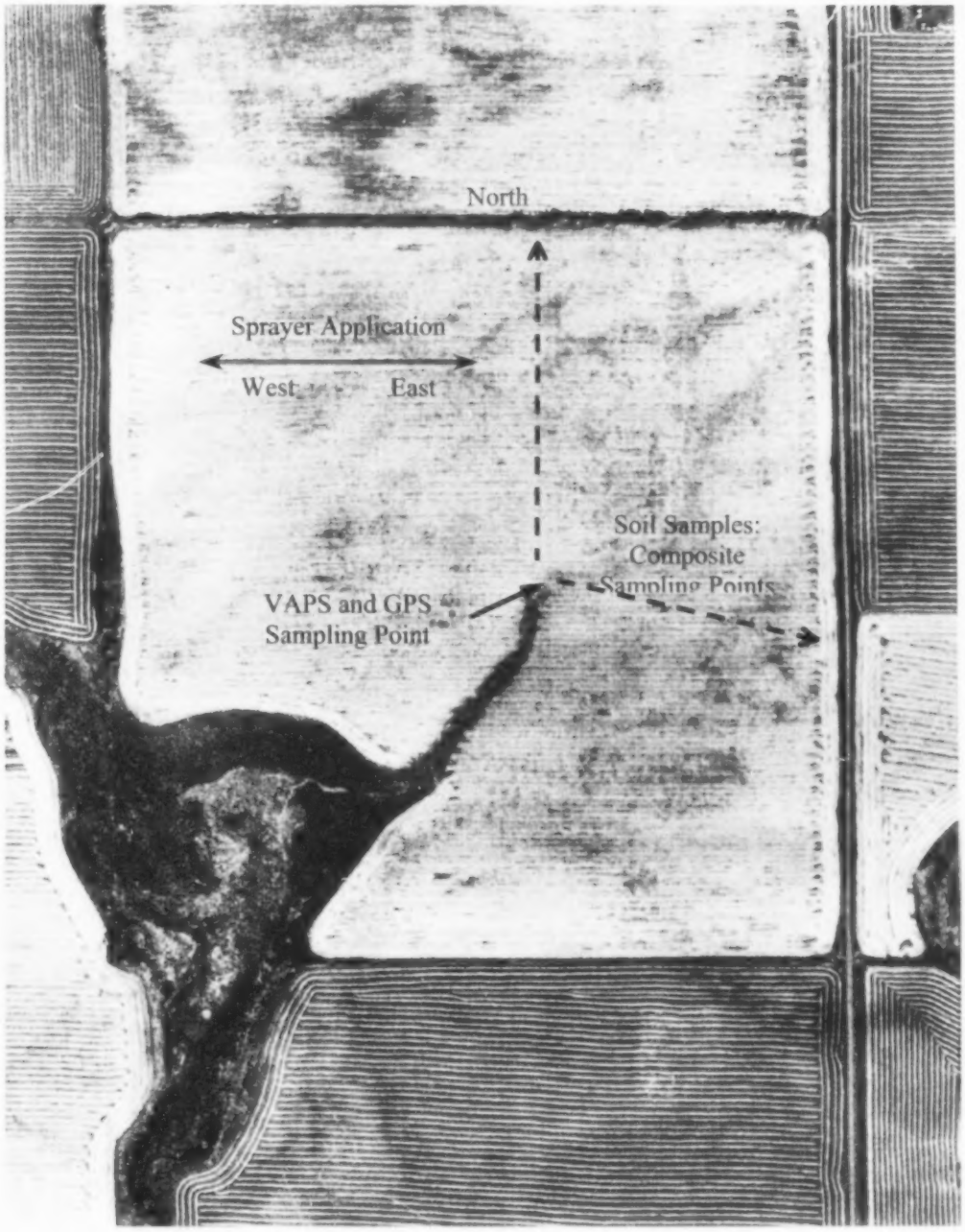
Vegreville sampling site: glass in foreground, plastic further away, 3 stakes where stability study containers were set out.

Appendix 3 **Parlby Atmospheric Deposition Site**
(Sampler in foreground)



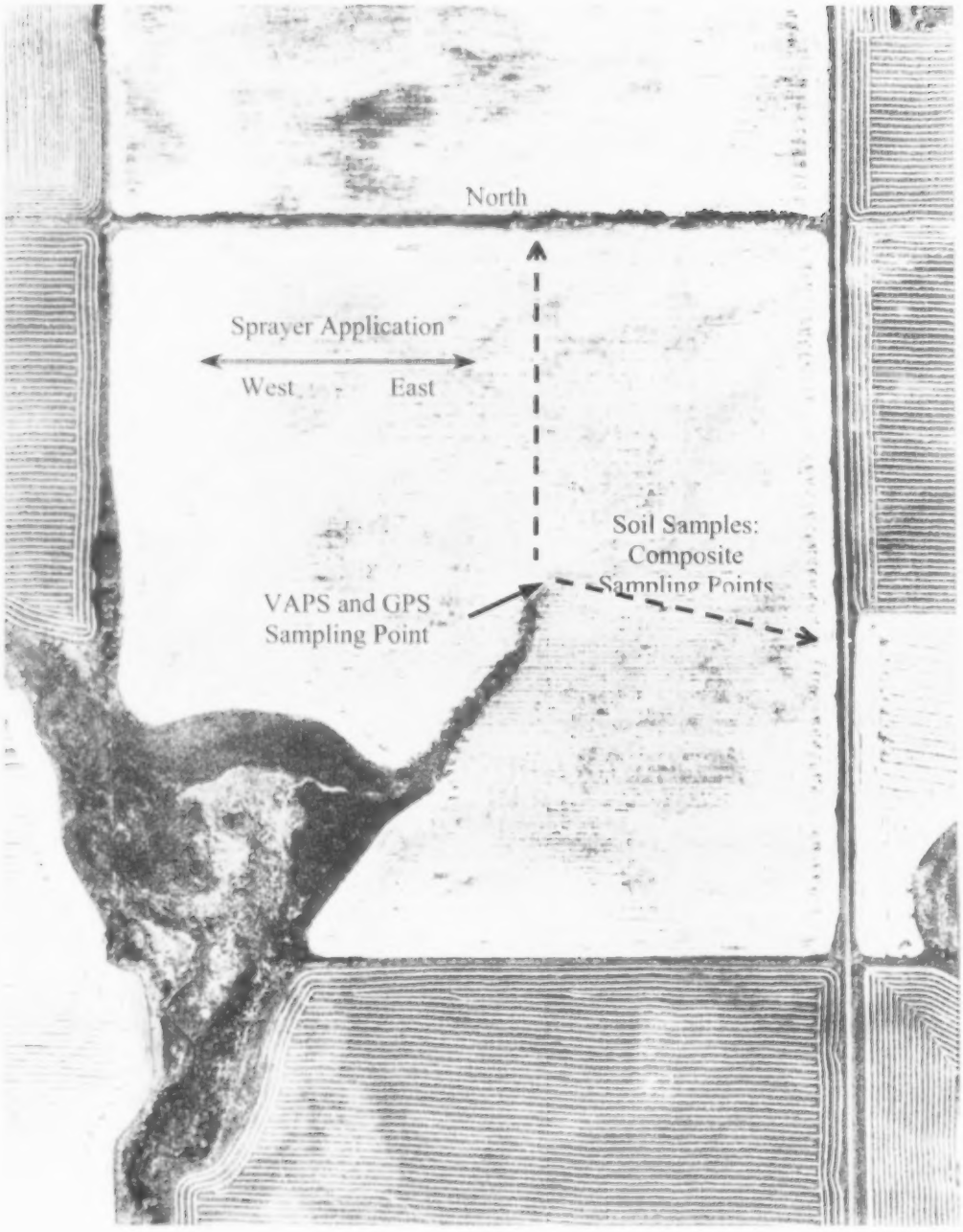
Appendix 4 Spray Event Pictures

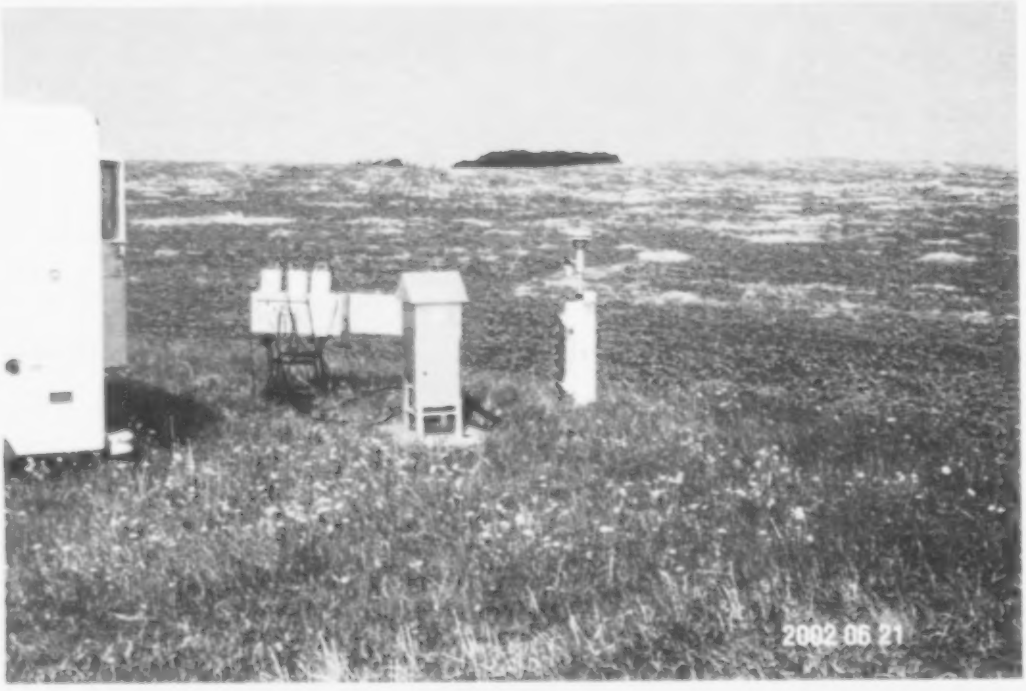
Spray Event Sampling Information
NE16-51-8-4



Appendix 4 Spray Event Pictures

Spray Event Sampling Information
NE16-51-8-4





From left: VAPS, GPS and weather station

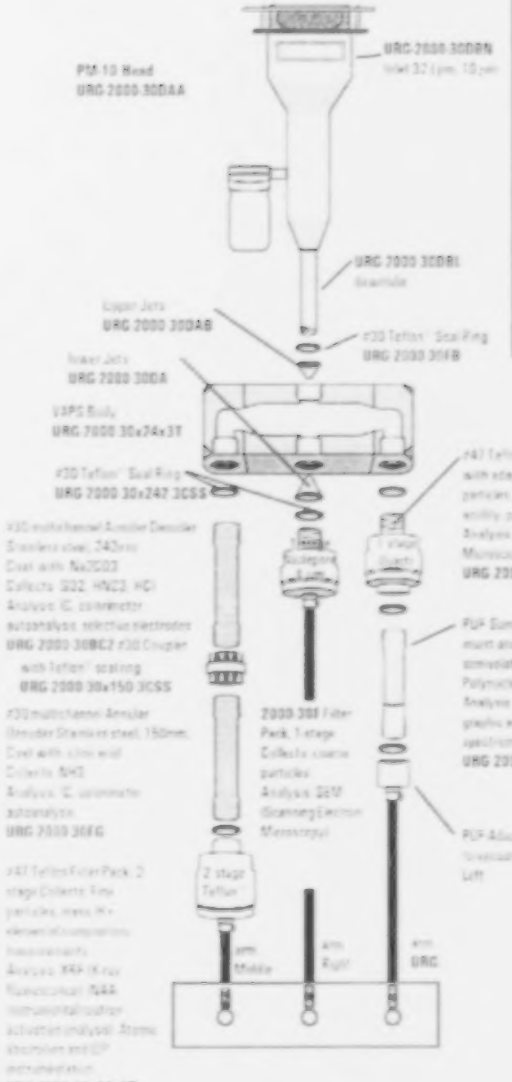
2002 06 21

2002 06 21

Appendix 5 Spray Event Sampling Equipment

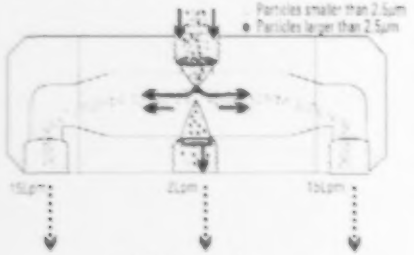
URG-3000K and URG-3000H2 Internals

URG-3000H2 Dual VAPS has two sets of internals

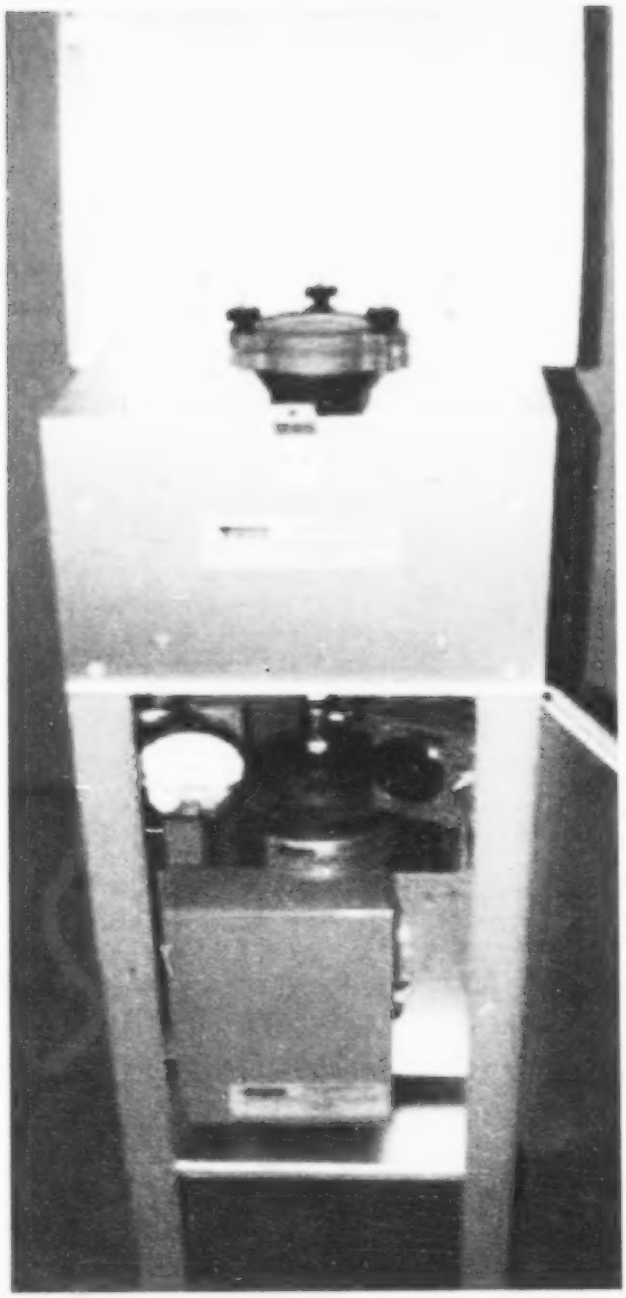


INSIDE THE VIRTUAL IMPACTOR

Larger particles entering the Virtual Impactor of the VAPS flow downward and collect on a Nuclepore filter. Smaller particles follow the two airstreams that flow at 15 Lpm and collect on Teflon or Quartz filters.



GPS Air Sampling Equipment



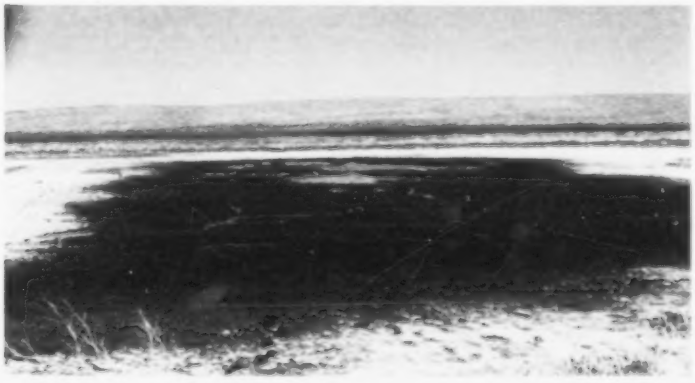
Appendix 6 Wetlands #10, #5, #51

Wetland # 10

May 16, 2002

May 29, 2002

June 12, 2002



Wetland # 5
May 16, 2002

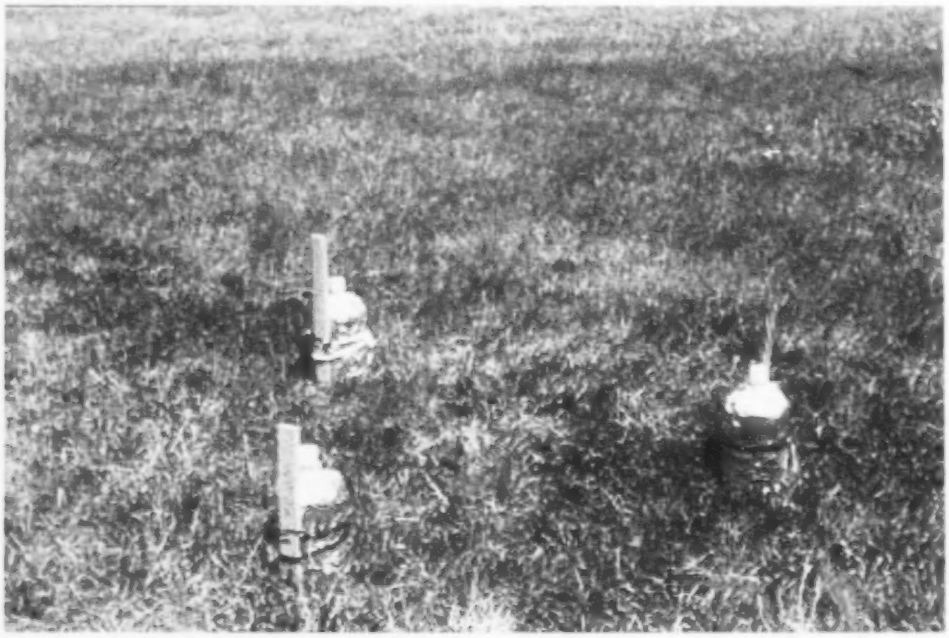
Wetland # 51
May 15, 2002

Appendix 7 Field Stability Study

Residue breakdown over time was documented under field conditions to establish the most desirable sampling frequency (i.e., collecting field samples before compounds degrade and concentrations decline).

Three 4L plastic sample bottles were installed at the Vegreville site near the regular atmospheric deposition collectors. The 3 bottles were filled with 500 mL nano-pure water spiked with glyphosate @ 4 µg/L, AMPA @ 20 µg/L and glufosinate @ 20 µg/L. No particulate matter was introduced into the spiked solutions. Sub-samples were drawn weekly.

Photo represents the sample bottles used to measure residue stability at the Vegreville site



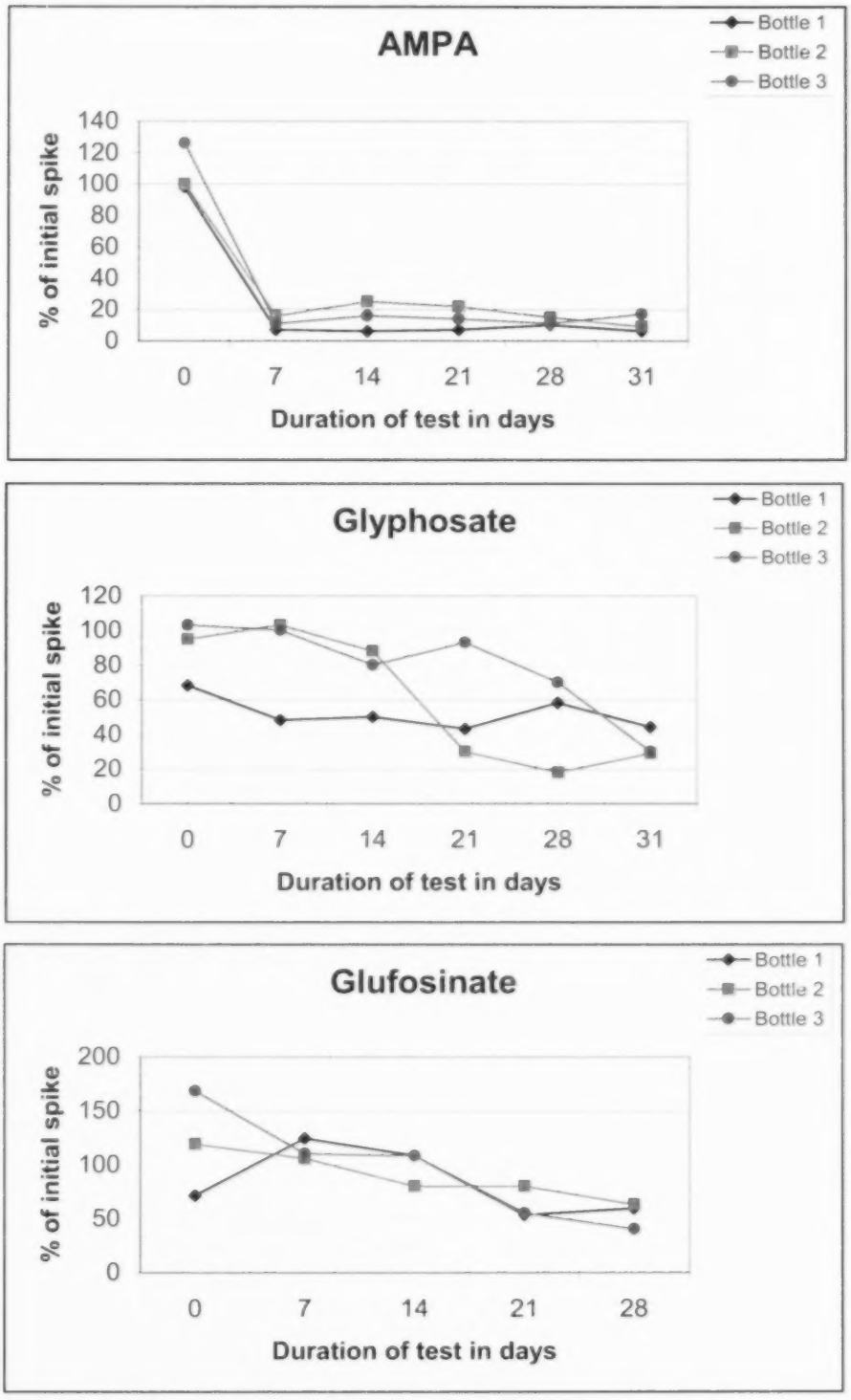
The results of the field stability test are presented in Table A7 and Figure A7.

AMPA appears to deteriorate almost immediately after introduction to field conditions. Daily sampling in the initial 7 days would help narrow down the maximum desirable sampling interval. This apparent immediate loss of AMPA coupled with a relatively high detection limit may explain why no AMPA was detected in any samples. Particulate matter in real samples may alter the rate of AMPA loss. It may be that AMPA breaks down in water more readily than in soil. Although measurable concentrations of AMPA persisted till the end of the study, concentrations declined very rapidly after start of testing and apparently more rapidly than the literature indicates. Giesey et al (2000) report a half-life for AMPA of 7-14 days while others (Goldsborough and Brown 1993) specify detections in water for 14 days after application.

Table A7. Breakdown of AMPA, glyphosate and glufosinate spikes exposed to field conditions

	Days	Date	Bottle 1		Bottle 2		Bottle 3	
AMPA			ug/L	%Remaining	ug/L	%Remaining	ug/L	%Remaining
	0	15-May	19.5	*98*	20	*100*	25.1	*126*
	7	22-May	1.5	*7*	3.2	*16*	2.1	*11*
	14	29-May	1.2	*6*	5	*25*	3.2	*16*
	21	5-Jun	1.3	*7*	4.4	*22*	2.8	*14*
	28	12-Jun	1.9	*10*	3	*15*	2.1	*11*
	31	19-Jun	1.2	*6*	1.7	*9*	3.3	*17*
			initial spike at 20 ug/L in nano-pure water					
Glyphosate								
	0	15-May	2.7	*68*	3.8	*95*	4.1	*103*
	7	22-May	1.9	*48*	4.1	*103*	4	*100*
	14	29-May	2	*50*	3.5	*88*	3.2	*80*
	21	5-Jun	1.7	*43*	1.2	*30*	3.7	*93*
	28	12-Jun	2.3	*58*	1.9	*18*	2.8	*70*
	31	19-Jun	1.74	*44*	1.2	*29*	1.2	*30*
			initial spike at 4 ug/L in nano-pure water					
Glufosinate								
	0	15-May	14.2	*71*	23.8	*119*	33.6	*168*
	7	22-May	24.8	*124*	21.2	*106*	21.9	*110*
	14	29-May	21.5	*108*	16	*80*	21.6	*108*
	21	5-Jun	10.6	*53*	15.9	*80*	10.9	*55*
	28	12-Jun	11.8	*59*	12.6	*63*	7.9	*40*
	31	19-Jun			No data			
			initial spike at 20 ug/L in nano-pure water					

Figure A7. Breakdown of AMPA, glyphosate and glufosinate spikes exposed to field conditions



AMPA may behave differently in distilled water (i.e., shorter half-life) than in natural water samples, which normally contain some particulate matter. Spiking of natural water samples may provide a more realistic idea of the stability of AMPA.

Notable differences were observed in glyphosate and AMPA concentrations measured in the three bottles. This could be the result of a spiking analytical measurement error, or an abnormality with the plastic sample bottles used. Glyphosate appears to remain stable for 14 days under field conditions. Daily sampling between 14 and 21 days would provide additional data to more accurately determine the maximum desirable sampling interval.

There were rather large differences in glufosinate concentrations initially recorded for the three bottles. These may be due to differences in spikes dispensed to the three bottles, but could also be indicative of variability in method accuracy. However, trends over time are similar among the three bottles and glufosinate appears to be stable for 14 days.

It is possible that particulate matter found in a surface water sample would stabilize concentrations of AMPA by binding the compound. Furthermore, use of a buffer solution in the sample container at the start of the sampling interval may help tie up the three compounds tested in this study and thereby allow an increase in acceptable sampling interval. Further studies need to be done on these aspects of sampling total precipitation (rain and dust). The determining compound for optimum sampling times is the glyphosate metabolite AMPA, since its deterioration appears to occur rapidly.

Appendix 8 Comparison of Suitability of Glass and Plastic Bottles

At the Vegreville site atmospheric deposition was collected throughout the growing season in pairs of glass and plastic bottles to determine the suitability of glass bottles for glyphosate sampling. Results of the paired sampling are presented in Table A8.

Table A 8. Comparison of Concentrations Measured in Glass and Plastic Bottles

Container Type	Start Date	End Date	# Days	µg/m^2/day	µg/L
glass	15-May	22-May	7	0.27	0.26
plastic	15-May	22-May	7	0.49	0.42
glass	22-May	29-May	7	0.90	2.60
plastic	22-May	29-May	7	0.61	1.80
glass	29-May	5-Jun	7	0.076	4.40
plastic	29-May	5-Jun	7	0.049	2.80
glass	5-Jun	12-Jun	7	0.061	3.60
plastic	5-Jun	12-Jun	7	0.139	5.60
glass	12-Jun	19-Jun	7	3.50	1.36
plastic	12-Jun	19-Jun	7	2.34	0.80
glass	19-Jun	26-Jun	7	0.034	0.23
plastic	19-Jun	26-Jun	7	0.103	0.65
glass	26-Jun	3-Jul	7	<0.007	<0.02
plastic	26-Jun	3-Jul	7	<0.007	<0.02
glass	3-Jul	17-Jul	14	0.027	3.20
plastic	3-Jul	17-Jul	14	0.027	3.20
glass	17-Jul	24-Jul	7	0.069	0.20
plastic	17-Jul	24-Jul	7	0.321	1.09
glass	24-Jul	31-Jul	7	<0.007	<0.05
plastic	24-Jul	31-Jul	7	<0.007	<0.05
glass	31-Jul	7-Aug	7	<0.007	<0.01
plastic	31-Jul	7-Aug	7	<0.007	<0.01

A paired t-test, used to compare the two series of measurements, revealed no significant differences in glyphosate concentrations or loadings between glass and the plastic sample bottles (glyphosate ($\mu g/m^2/day$): paired t-test $p = 0.83$; Glyphosate ($\mu g/L$): paired t-test $p = 0.87$).

This suggests that for glyphosate sampling either plastic or glass bottles can be used. The suitability of glass bottles for AMPA and glufosinate was not tested in this experiment.

Appendix 9 Results of QA/QC Sample Analyses

9.1 PUF Extraction Study

A PUF spiking study was undertaken to determine the extractability of glyphosate, AMPA, and glufosinate from the PUF medium. The PUF medium was spiked with 2000 ng glyphosate /PUF, 10,000 ng AMPA /PUF and 10,000 ng glufosinate /PUF.

Three - 2.5 x 10 cm spiked PUFs were extracted with the soil extractant solution ammonium hydroxide/ phosphate buffer solution using an ultrasonic bath. No post extraction concentration was done. Extracts were analyzed, without cleanup, by the in situ derivatization method used for precipitation and water samples. The first extraction used 50 mL extraction solution while the second and third used 30 mL solution.

Results are presented in Table A9.

Table A9 Recovery of glyphosate, AMPA and glufosinate in PUF samples

Spike	Compound	Recovery
#1	Glyphosate	110%
(50mL extract)	AMPA	0%
	Glufosinate	398%
#2	Glyphosate	72%
(30mL extract)	AMPA	0%
	Glufosinate	150%
#3	Glyphosate	112%
(30mL extract)	AMPA	32%
	Glufosinate	116%
Average	Glyphosate	98%
	AMPA	10.7%
	Glufosinate	221%

Excellent recoveries were achieved for glyphosate in PUF media. AMPA and glufosinate had poor or inconsistent recoveries. As the overall study was exploring glyphosate release into the environment, the PUF samples collected for the field study were not analyzed for the other two components. Further studies need to be done to determine the causes of the poor or inconsistent results for AMPA and glufosinate.

9.2 Surface Water Samples

To assess the overall data quality resulting from sampling and analytical procedures, QA/QC samples were an integral part of the surface water sampling program and included blank, split and spiked samples that were submitted blind to the laboratory.

Blanks

Field Blank	12-Jun-02	<0.2 µg/L
Field Blank	23-Jul-02	0.2 µg/L
Field Blank	14-Aug-02	<0.2 µg/L
Field Blank	04-Sep-02	<0.2 µg/L

Field blank samples give an indication of false positive results being generated by the laboratory and of contamination during sample handling. Three of the four samples yielded concentrations less than MDL. However, one sample with a reported concentration at the MDL appears to be a false positive.

Splits

Wetland #51	12-Jun-02	<0.2 µg/L
Wetland #51	12-Jun-02	<0.2 µg/L

Split samples provide a general indication of the precision of measurements. Both samples of the single split sample analyzed had concentrations less than MDL.

Spikes

Wetland #51	12-Jun-02	0.05 µg/L spike value 0.5µg/L	recovery = 10%
Unspiked split	29-Jul-02	0.1 µg/L	
Spiked split	29-Jul-02	0.5 µg/L split + spike value 1.0 µg/L	recovery = 40%
Unspiked split	24-Sep-02	<0.2 µg/L	
Spiked split	24-Sep-02	<0.2µg/L split + spike value 0.5 µg/L	recovery = 0%

Spiked samples help evaluate the accuracy of measurements. Three split/spiked samples were sent to the laboratory over the sampling season. Spiked recoveries were low with the average recovery being 17% (range 0 – 40%). The low recoveries would indicate that the database for surface water samples is biased low and that actual concentrations are likely higher than reported. Another possible explanation would be that the spiked glyphosate was bound with the particulate or organic matter and was not extracted by the water analysis method.

Overall results of the QA/QC sample analyses indicate that glyphosate data reported for surface waters are probably fairly conservative: few false positive detections were reported based on the field blanks analyzed and based on the large number of concentrations reported as less than the method detection limit (MDL); spikes consistently were reported at concentrations which were below the spike design concentrations. These results suggest that reported concentrations tend to underestimate concentrations measured in rich organic waters typical for streams and wetlands in agricultural areas.